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Kenneth J. Wynne

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IONIC COMPLEXES OF CONJUGATED OLIGOQUINOLINES

ASHOK S. SHETTY AND SAMSON A. JENEKHE

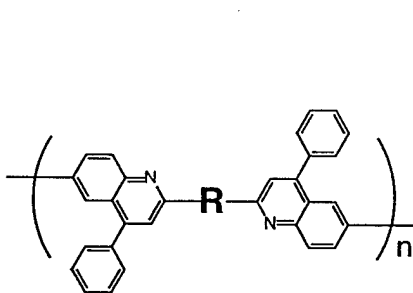
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ABSTRACT

Single crystal X-ray structures of salt complexes of oligoquinoline, 2,2'-bis(4-phenylquinoline)-1,4-phenylene (4), with *p*-toluenesulfonic acid, trifluoromethanesulfonic acid and a laser dye, Sulforhodamine 101 hydrate have been determined and used to study the effects of molecular packing on physical and photophysical properties of conjugated oligomer and polymers. UV-vis and emission spectra of thin films of the oligoquinoline-*p*-toluenesulfonate complex were also performed. These results indicate that they form an intermolecular charge-transfer complex. These complexes serve as models of quarternized polyquinolines such as the self-assembled bilayer films of polyquinoline and polystyrenesulfonic acid.

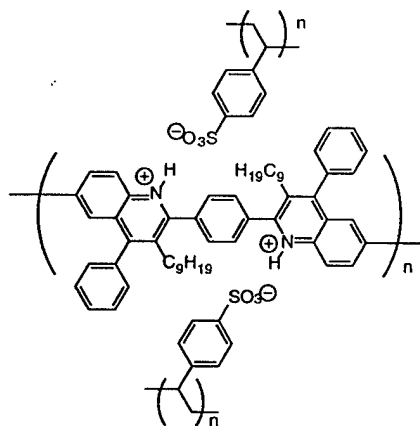
INTRODUCTION

Conjugated polymers are the subject of much research effort because of their potential applications in electronic, optoelectronic, and optical devices [1]. One class of conjugated polymers that we have extensively investigated are the conjugated rigid-rod polyquinolines, with the general structure 1, because of their excellent thermal stability and high mechanical strength. They are also intrinsic n-type (electron transport) semiconducting polymers [2] with interesting electronic [3], photoconductive [4], and nonlinear optical [5] properties. Recently, they were also used as both the electron-transport layer and the emission layer in polyquinoline/poly(*p*-phenylenevinylene) heterojunction light-emitting diodes (LEDs) [6].



1

R = aromatic groups



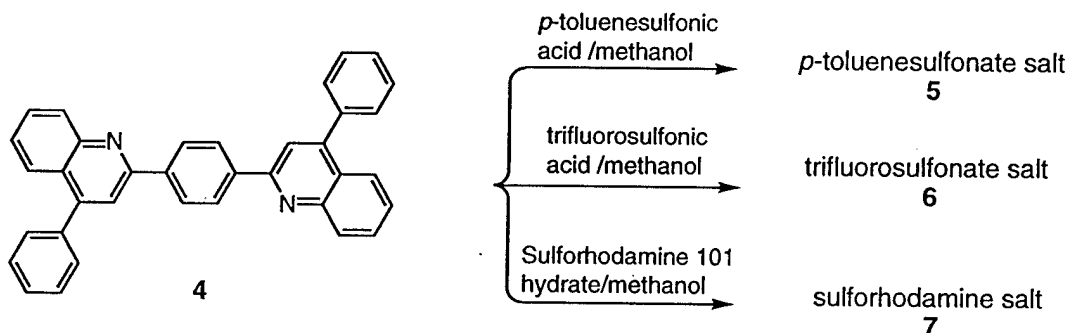
BuN-PPQ (2).PSSA (3)
complex

Precise control over the molecular and supramolecular organizations of these polymeric materials could enhance the efficiency and overall performance of the devices they are incorporated in [7]. One of the methods that exemplifies this approach is the construction of layer-by-layer thin films by consecutively alternating adsorption of oppositely charged polyelectrolytes from dilute solutions [8,9]. The advantage of this

method is that the thickness and supramolecular architecture of thin films could be controlled very precisely. Multilayer thin film materials have been successfully fabricated in this way with a large variety of polymers, such as conjugated [10] and non-conjugated [8,9] polyions, conjugated polymer precursors [11,12], and p-type doped conducting polymers [7].

We have recently used this method for the construction of bilayer films of polyquinoline, poly(2,2'-(*p*-phenylene)-6,6'-bis(3-nonyl-4-(*p*-*tert*-butyl phenyl)quinoline)) (BuN-PPQ, **2**), and polystyrenesulfonic acid (PSSA, **3**) [13]. This was accomplished by dipping thin films of the polyquinoline into a dilute solution of PSSA in methanol. The sulfonic acid groups of **3** formed an acid-base complex with the imine nitrogens of the polyquinoline leading to the adsorption of PSSA onto the polyquinoline layer. This adsorption was monitored using optical absorption and photoluminescence spectroscopies. The photoluminescence emission efficiency of the polyquinoline/PSSA complex was enhanced by over one order of magnitude, suggesting that such complexes are promising candidates for incorporation into optoelectronic devices.

To gain a better understanding of the polyquinoline/PSSA complex and quarternized polyquinolines in general, on a molecular and supramolecular level, we initiated investigation of complexes of oligoquinolines with various sulfonic acids. Results for oligoquinoline 2,2'-bis(4-phenylquinoline)-1,4-phenylene (**4**) which is the model for polyquinoline and its complexes are reported here. Photophysical studies and X-ray structures of single crystals of these complexes together with their photophysical properties provide a good basis for understanding the molecular structure and properties of the polyquinoline complexes in particular and polyelectrolyte complexes in general. To our knowledge, this comprises the first such study.



EXPERIMENTAL SECTION

Materials. All the starting materials were obtained from Aldrich and used as received. The oligoquinoline **4** was synthesized by condensing 2-aminobenzophenone and 1,4-diacetylbenzene in a *m*-cresol:diphenylphosphate mixture [14]. It was recrystallized from a methanol/THF mixture prior to use. Sulfonate salts were prepared by dissolving stoichiometric amounts of oligoquinoline **4** and the corresponding sulfonic acid in methanol. Single crystals of the complexes were obtained by the slow evaporation of the methanol.

Characterization. Crystals of **5**, **6** and **7** were each cut and mounted under Paratone-8277 on glass fibers, and immediately placed on the X-ray diffractometer in a cold nitrogen stream supplied by a Siemens LT-2A low temperature device. The X-ray intensity data were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). Thin films of the complexes were prepared by spin coating of the methanol solutions. Optical

absorption spectra were recorded with a Perkin-Elmer Model Lambda 9 UV-Vis-NIR spectrophotometer. Steady state photoluminescence spectra were recorded by using a Spex Fluorolog-2 spectrofluorometer equipped with a Spex DM3000f spectroscopy computer.

RESULTS AND DISCUSSION

The molecular and single-crystal X-ray structures of the complex **5** are shown in Figure 1. In the crystal structure, the complex is located on a crystallographic center of symmetry at the midpoint of the central 1,4-biphenylene ring of the oligoquinoline as would be expected. The quinoline moieties are in a crystallographically imposed *anti*-orientation with respect to each other. The *p*-phenylene ring is twisted 21° from the mean plane of the quinoline moieties. The phenyl groups appended onto the quinoline moieties in the oligomer, are twisted at *ca.* 50° from each of the quinolines. The *p*-toluenesulfonate moieties are oriented such that the tolyl groups form an "edge-to-face" π -stacking interaction [15] with the central *p*-phenylene ring of the oligoquinoline. Hence they are predisposed to engage in an intermolecular charge-transfer interaction between the sulfonates and the oligoquinoline moiety. This is reflected in the photophysical properties of thin films of the complex (Figure 2).

The UV-vis absorption maximum of the complex (370 nm) is red shifted by 20 nm compared to the pure oligoquinoline **4** (350 nm). The emission spectra (Figure 2), display a red shift of 50 nm between the peak maxima of **4** (420 nm) and **5** (470 nm). As the peaks in the absorption and the emission spectra cannot be assigned simply to a π - π^* transition, the above observations indicate that there is a intermolecular charge transfer component between the negatively charged sulfonates and the positively charged oligoquinoline. UV-vis and emission studies of the solution of the complex could not be accomplished as they dissociate in solution. The photophysical and X-ray structural studies of the oligoquinoline:*p*-toluenesulfonic acid complex (**5**), which may be considered to be the model compounds of the polyquinoline BuN-PPQ (**2**):PSSA (**3**) complex, indicate that there could be similar charge-transfer between the two polymers which could account for the enhanced quantum efficiency and the bathochromic shift in the emission spectra of the complex.

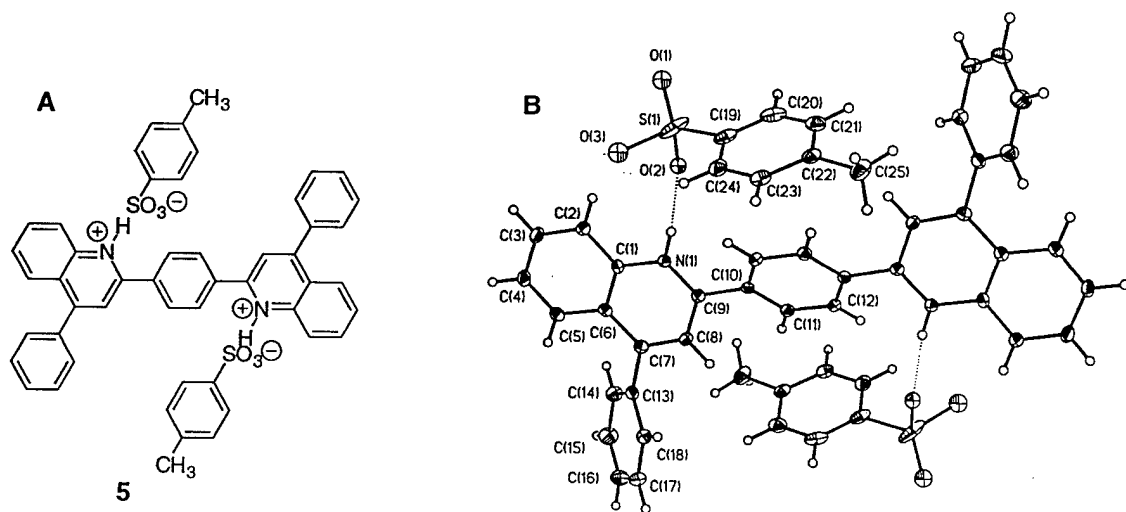


Figure 1. Molecular structure (A) and 30% ORTEP diagram (B) of **5** with the atom numbering. The dotted line represents the hydrogen-bonding between the oxygen atom of the *p*-toluenesulfonate molecules and the protonated nitrogens of the oligoquinoline.

To further study the effects of the anion structure on intermolecular charge-transfer, we studied complexes of the **4** with trifluoromethyl sulfonic acid (**6**) and with Sulforhodamine 101 Hydrate (**7**). In the former salt, we expected a diminished intermolecular charge transfer because of the absence of aromatic groups on the sulfonate. In the case of **7** we expected enhanced charge transfer interaction with **4** because of the highly conjugated nature of the sulforhodamine. The molecular structure of the complexes are shown in Figures 3 and 4. In the crystal structure of **6**, the complex is located on a crystallographic center of symmetry at the midpoint of the central 1,4-phenylene ring of the oligoquinoline. The quinoline moieties are in a crystallographically imposed anti-orientation with respect to each other. The *p*-phenylene ring is twisted 25° to the mean plane of the quinoline moieties. The phenyl groups appended onto the quinoline moieties in the oligomer, are twisted *ca.* 65° to each of the quinolines. However, in this case, two methanol molecules participate in the hydrogen bonding as is shown in Figure 3. Thus the methanols play a key role in stabilizing the crystals. On exposure to air, the crystals crumble on the loss of the methanol molecules. The trifluoromethane sulfonates are oriented such that the oxygen atoms are at *ca.* 3 Å from the *p*-phenylene ring indicating there is an interaction between the electron deficient *p*-phenylene ring and the sulfonates

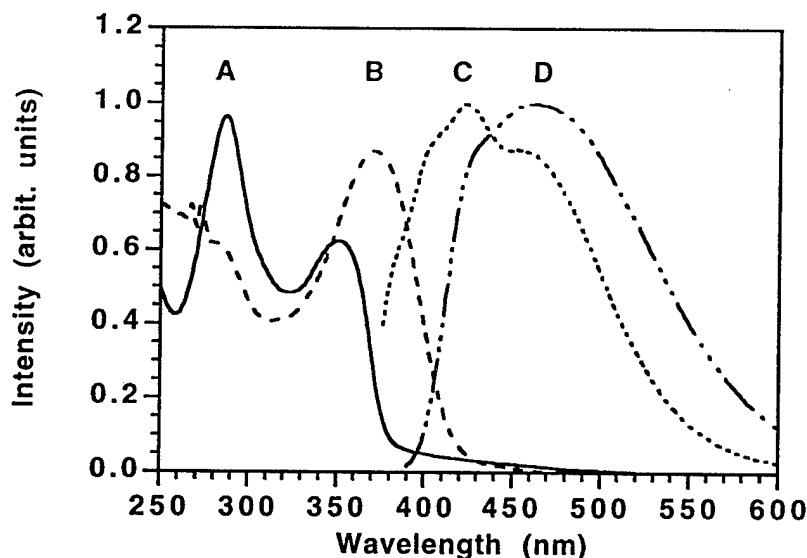


Figure 2 : UV-vis fluorescence spectra of thin films of oligoquinoline **4** and its *p*-toluenesulfonate salt **5**.

UV-vis

oligoquinoline **4** (curve A)

p-toluenesulfonate salt **5** (curve B)

Emission

oligoquinoline **4** (curve C)

p-toluenesulfonate salt **5** (curve D)

In the crystal structure of **7**, the salt molecule is not located on a crystallographic center of symmetry at the midpoint of the central 1,4-phenylene ring of the oligoquinoline as would be expected. The quinoline moieties are in a crystallographically imposed anti-orientation with respect to each other. The *p*-phenylene ring is twisted at 25° to the mean plane of the quinoline moieties. The phenyl groups appended onto the quinoline moieties in the oligomer, are twisted at *ca.* 45° to each of the quinolines. The sulforhodamine is π -stacked with the quinoline moieties of the oligoquinoline. Eight methanol molecules are in

the unit cell and hold the integrity of the crystal. The crystals crumble on exposure to air on losing the methanols. Photophysical studies these complexes are in progress.

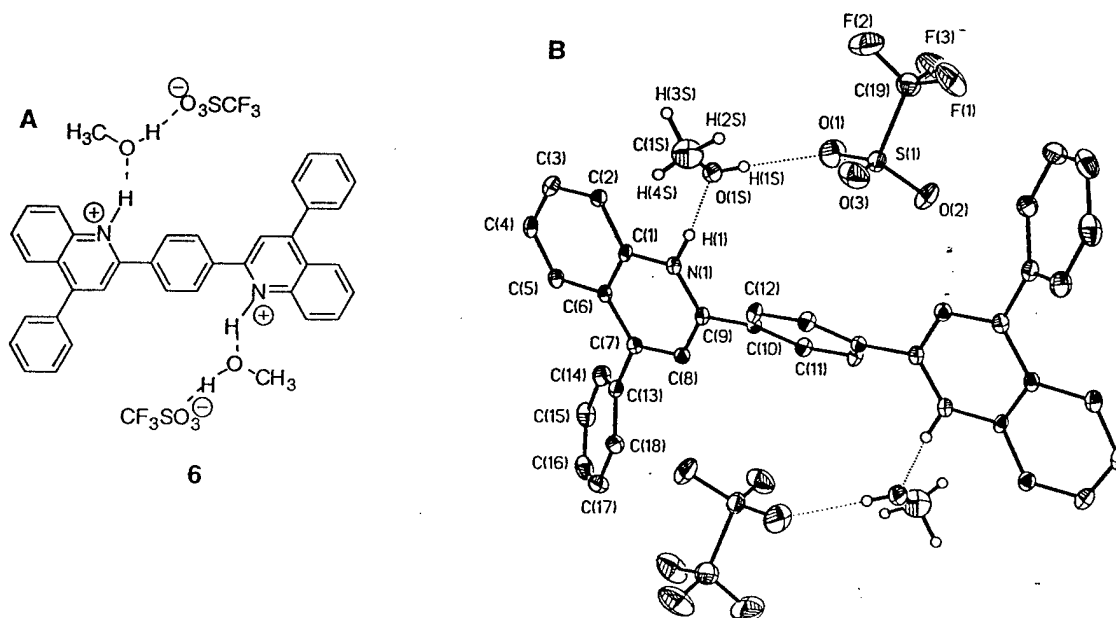


Figure 3. (B) 30% ORTEP diagram of **6** with the atom numbering. The dotted line represents the hydrogen-bonding between the oxygen atom of the trifluoromethane sulfonate molecules, the methanols, and the protonated nitrogens of the oligoquinoline.

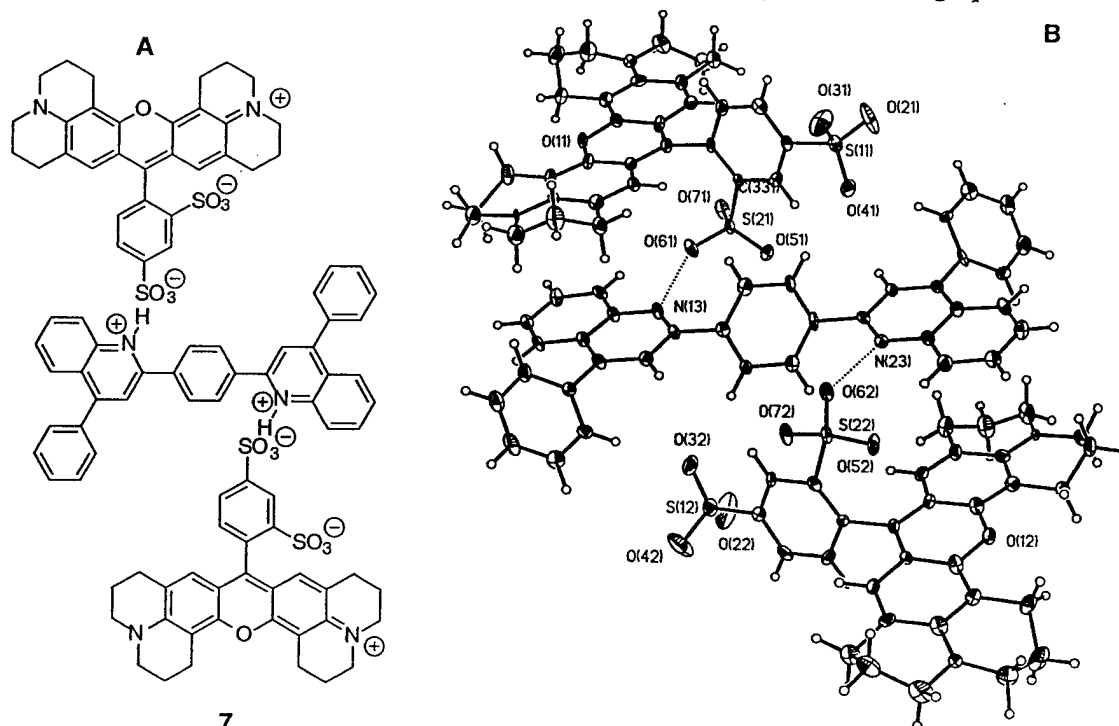


Figure 4. (B) 30% ORTEP diagram of **7** with the numbering of the selected atoms. The dotted line represents the hydrogen-bonding between the oxygen atom of the sulforhodamine molecules and the protonated nitrogens of the oligoquinoline. The eight methanol atoms have been omitted for clarity.

CONCLUSIONS

We have synthesized new complexes of oligoquinolines with various sulfonic acids and determined their X-ray crystal structures. We have also performed photophysical studies of one of these complexes which indicate there could be a significant intermolecular charge transfer between the negatively charged sulfonates and the positively charged oligoquinoline. These complexes serve as electronic models of the self-assembled bilayer films of polyquinoline, BuN-PPQ **2** and PSSA **3** and the results from studies on the model complexes indicate that there could be charge-transfer between the two polymers in particular and polyelectrolyte complexes in general.

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